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Rheology and Thermotropic Properties of Bis-Urea-Based Organogels in Various Primary Alcohols

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The thermotropic and viscoelastic properties and the structure of thermoreversible organogels composed of enantiomerically pure *trans*-1,2-bis(3-dodecylureido)cyclohexane (**1**) and primary alcohols, i.e., propanol, butanol, hexanol, and octanol, have been investigated by melting-point measurements, differential scanning calorimetry (DSC), rheology, and electron microscopy. The electron microscopic studies revealed that gelation of these solvents occurred through the formation of an entangled network by **1**. In all solvents, the gels behave as viscoelastic solids, with $G' \gg G''$ at frequencies >0.01 Hz (time scales <100 s) and values of G' up to 500 kPa (50 mM in propanol). The thixotropic character of the gels, however, indicates that the network structure is dynamic at larger time scales. Although the structure of the gels in these solvents is not significantly different, both the thermal stability and the strength of the gels depend on the solvent, and they increase in the order octanol < hexanol < butanol < propanol. It was concluded that solvophobic effects become important for the stabilization of gels of **1** in more polar solvents.

Introduction

Organogelators are small organic molecules that, already at low concentrations, turn a liquid into a gel.[1] Well-known gelling agents include, for instance, certain cholesterol and anthracene derivatives,[2] surfactants,[3] porphyrins and phthalocyanines,[4] carbohydrate[5] and peptide derivatives,[6] and bis-urea compounds.[7,8] The enormous structural diversity among these gelling agents, together with the fact that structurally closely related compounds do not exhibit any gelation ability, has meant that most studies on organogelators have focused on the structural aspects of the gelation process. A common trait among these molecules appeared to be that they self-assemble through highly specific noncovalent interactions into long fibrous structures, which in turn form an entangled network in the liquid. The presence of strong self-complementary and unidirectional intermolecular interactions has thus clearly been identified as a molecular prerequisite for gelation ability,[1] and this criterion has been used for the design of novel organogelators by several groups, including ours.[2d,5e−f,6c,7,8] However, many other aspects of gelation phenomena by small organic gelling agents are still poorly understood. This concerns especially the viscoelastic properties of organogels, which are in fact among the most prominent characteristics of gel systems in general. These properties have led to many applications of gelling agents as rheology modifiers or structuring agents in different areas ranging from oil recovery to pharmaceutical products. Pioneering work in this area has been done by Terech, who carefully characterized different organogel systems by rheology.[9] It was found that organogels behave either as viscoelastic liquids or as viscoelastic solids, which is due to the formation of a highly dynamic or a static network structure, respectively.

The bis-urea cyclohexane-based gelling agents such as **1** have recently been introduced, first by Hanabusa and later also by our group (Scheme 1); they form thermoreversible gels with many different organic solvents already at low concentrations.[7a,8bc] These novel gelling agents have the distinct advantage that they are easy to synthesize and that many structural variations of *R* are allowed, and therefore they are excellent model compounds with which to study gelation phenomena in more detail. In addition to the structure of the gelling agent, the gelation ability

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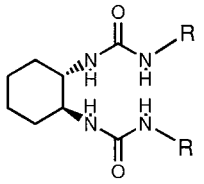
Scheme 1



1: R = -$C_{12}H_{25}$

and properties of the gels also depend on the nature and properties of the solvent. In particular, the relationship betwee gel and solvent properties is even less understood than the relationship between structure and gelation capability. A suitable set of solvents with which to study solvent effects in more detail is, for instance, a homologous series of alcohols. These offer a wide range of different polarities, but all have the same functionality, acting as both hydrogen-bond donor and acceptor.[10] Here we report on the thermotropic behavior and rheological properties of gels of a cyclohexyl bis-urea gelling agent, i.e., enantiomerically pure *trans*-1,2-bis(3-dodecylureido)cyclohexane (**1**), in a series of primary alcohols. We will discuss the results in relation to the structure of the gels and the properties of the solvents.

Experimental Section

Preparation of the Gels. The organogelator *(R,R)*-1,2-bis-(3-dodecyl-ureido)cyclohexane was prepared as described previously.[8c] The solvents 1-propanol, 1-butanol, 1-hexanol, and 1-octanol were of analytical grade and were used as received. For the preparation of the gels, the solvent and the organogelator (0.5−5 w/v %) were heated in a closed vial until a clear solution was obtained. When the solution had cooled to room temperature, a gel was formed.

Electron Microscopy. For electron microscopy, a piece of the gel was deposited on a Formvar/carbon-coated copper grid (400 mesh) and removed after 1 min, leaving some small patches of the gel on the grid. After being dried at low pressure ($<10^{-5}$ Torr), the specimen was shadowed at an angle of 45° with platinum. The specimen was examined in a JEOL 1200 EX transmission electron microscope operating at 80 kV. In studying the specimen, we first searched for patches of the gel to be sure that the observed structures originate from it. Micrographs were taken from structures at the periphery of the gel patches, because here the fibers are deposited in a layer thin enough to be observed by transmission electron microscopy.

Gel Melting Temperatures. For the dropping-ball experiments,[11] gels with a volume of 1 mL were prepared in vials with a diameter of 10 mm. After the gel had aged for at least 12 h at 0 °C, a steel ball with a diameter of 3 mm (ca. 110 mg) was placed on top of the gel, and the vial containing the gel was placed in an oil bath. The temperature of the oil bath was slowly increased (0.3−0.5 °C/min) while observing the position of the steel ball. The temperature at which the ball touched the bottom of the vial was taken as the melting temperature. The dropping-ball experiments were carried out at least twice, and the melting temperatures thus obtained were reproducible to within ±1 °C.

Differential scanning calorimetry. Differential scanning calorimetry (DSC) was carried out on a Perkin-Elmer DSC7. The bis-urea gelator (0.50 mg) and solvent (40 μL) were placed in a 60 μL stainless steel sample cup which was directly sealed. The sample cup was placed in the DSC apparatus together with an empty sample cup as reference. The cups were heated for 15 min at 100 °C, cooled at a rate of 5 °C/min to −10 °C, and aged for 15 min at this temperature. Heating and cooling scans were then recorded from −10 °C to 100 °C at a scan rate of 5 °C/min. Repeated heating and cooling scans of the same and of different sample preparations were highly reproducible, and higher cooling rates or prolonged aging times (up to 20 h) did not affect the results.

Rheological Characterization. Rheological characterization was performed using a controlled stress rheometer (Carrimed CSL500) equipped with a concentric cylinder measuring cell (dimensions: $r_{inner} = 13.83$ mm, $r_{outer} = 15.00$ mm, and height = 32 mm). The measuring cell was connected to a water bath for control of the sample temperature (±0.1 °C). A hot solution of the bis-urea compound was poured into the measuring cell of the rheometer and cooled to 20 °C in ca. 5 min. Subsequent gelation of the solution was followed by measuring dynamic moduli (G' and G'') as a function of time. The dynamic moduli were obtained from small-amplitude oscillatory measurements. The measurements were made at 1 Hz frequency and a stress amplitude of $\sigma_0 = 10-100$ Pa (within the linear regime). The evolution of G' and G'' was followed for ca. 10 h, after which G' and G'' were measured as a function of oscillation frequency. The frequency was changed from 0.1 to 4 Hz in 20 min. Subsequently, G' and G'' were measured as a function of stress amplitude. The amplitude was changed from 0 to 275 Pa in 20 min. In addition to oscillatory measurements, steady-shear viscosity measurements were performed. These measurements were made on solutions of the bis-urea gelling agent before gelation had occurred. Viscosity was measured at various shear rates (5, 10, 25, and 100 s^{-1}). All measurements were performed at 20 ± 0.1 °C.

Gelling Time. To determine the gelling time a gel was heated to 60 °C in a water bath until the gel had melted and a constant temperature had been reached. The sample was then taken out of the water bath and allowed to cool to room temperature in air, and inspected for gelation every 15−30 s by slightly turning the vial. When the meniscus no longer moved anymore upon turning of the vial, gelation was considered to have occurred. The gelling time, t_{gel}, was taken as the time elapsed between gelation and removal of the sample from the water bath.

Results and Discussion

Structure of the Gels. Bis-urea gelator **1** forms stable gels with a variety of alcohols, including 1-propanol, 1-butanol, 1-hexanol, and 1-octanol, when present at a concentration between approximately 0.5 and 5 (w/v) %. In these solvents the gels are optically transparent at low concentrations of the gelling agent, but at higher concentrations they become turbid. Light microscopy revealed that the gels are birefringent, which is indicative of the presence of well-ordered structures, but further structural details were not observed.

Figure 1 shows the electron micrographs of gels of **1** in various primary alcohols. From these micrographs it is clear that in these solvents the gelling agent is aggregated into elongated fibers, which form an entangled network, thereby immobilizing the liquid. Most of the fibers are tenths of micrometers long, with diameters up to 100 nm. It can be clearly seen that the thicker fibers are built up from thinner ones, and that the smallest resolved entity amounts to 15−20 nm, which is an order of magnitude larger than the molecular dimensions of **1**. In all solvents employed in this study, many of the fibers are twisted to form left-handed helices. The pitch of the helices is, however, not regular, indicating that twisting results from anisotropy of the interfacial energy rather than a helical packing at the molecular level.[8c,12] At irregular intervals the fibers fuse and split, leading to the formation of junction zones, which stabilize the three-dimensional entangled network structure. The electron micrographs of Figure 1 do not reveal clear differences in fiber dimensions and network structures for gels of 1-butanol, 1-hexanol, and 1-octanol. For gels in 1-propanol, however, the typical fiber length is 1−5 μm, which is significantly

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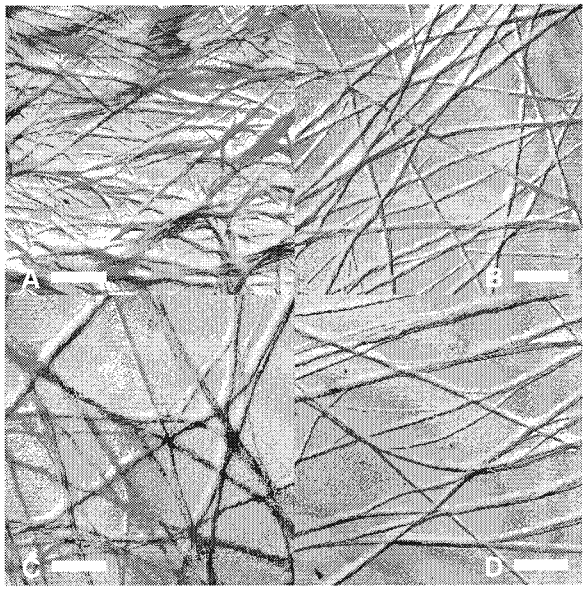

Figure 1. Transmission electron micrographs of gels of **1** in 1-propanol (a), 1-butanol (b), 1-hexanol (c), and 1-octanol (d). The concentration of **1** is in all cases 9 mM, and gels are aged for 16 h at 20 °C. The bar is 500 nm.

shorter than for the other solvents studied, and fibers tend to be more aggregated than in the other solvents.

Thermotropic Behavior. Gels of **1** are readily obtained upon cooling of an isotropic solution of **1** to room temperature. Upon heating, the gel melts to again form an isotropic liquid. This process can be repeated many times, indicating that gel formation is completely thermoreversible. The thermotropic behavior of the gels was studied by the dropping-ball method[11] and by DSC. In a dropping-ball experiment the gels are slowly heated while the position of a small steel ball on top of them is observed; this continues until, at a certain temperature, the gel no longer bears the ball. For gels of **1** in the primary alcohols studied here, a gradual lowering of the ball over a temperature trajectory of 5 to 10 °C was observed; therefore, the temperature at which the ball reaches the bottom of the vial is taken as the gel−sol phase transition temperature (T_g). We found that the reproducibility of the melting temperatures is better than 1 °C if heating of the gel is sufficiently slow, i.e., <2 °C/min. Because preliminary experiments revealed that the melting temperatures are rather close to room temperature, especially for the lower concentrations, the gels were aged at 0 °C and measurements were started at this temperature. Furthermore, it was observed that the melting temperatures initially increased with aging of the gels, until after several hours a constant melting temperature was obtained. Apparently, gelation of alcohols by **1** is a rather slow process and can take up to several hours, especially at lower concentrations. Rheology experiments (vide infra) revealed that even for the lowest concentrations, the gelation process is complete after 12 h, and therefore gels were aged for at least that long before their melting temperatures were measured. It should be noted that the aging period required to obtain a constant melting temperature depends on the concentration and on the temperature; however, this aspect was not studied in detail. The final melting temperature, however, did not depend on the aging temperature provided that the aging period had been long enough.

Phase diagrams of gels of **1** in the various alcohols are easily obtained from the concentration dependence of the gel−sol phase transition temperatures (T_g) (Figure 2). A

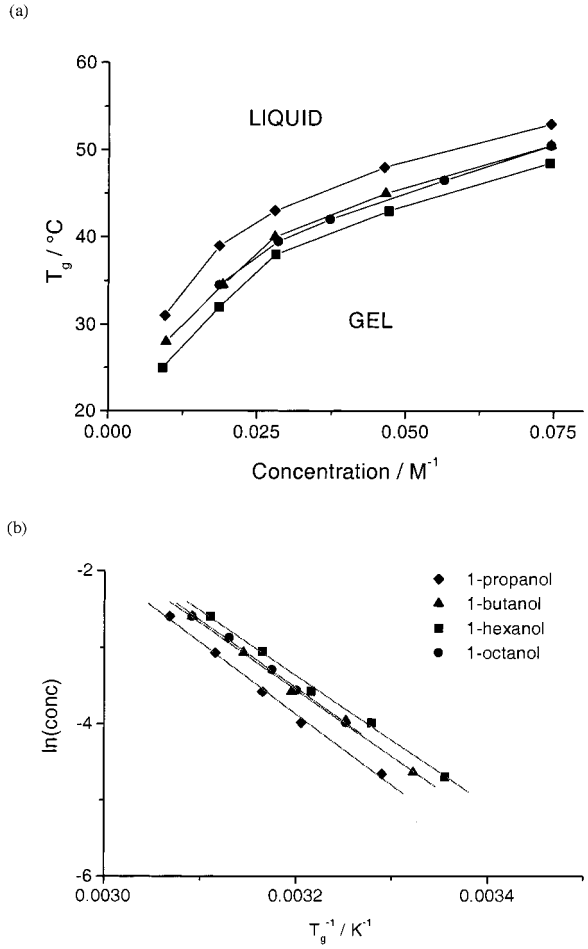

Figure 2. Binary phase diagrams of **1** with various primary alcohols (a) and the corresponding van't Hoff plots of the melting transition of the gels (b).

qualitative interpretation of the phase diagrams shows that the thermal stability of 1-octanol and 1-butanol gels of **1** is comparable, whereas the 1-hexanol gels are slightly less stable. The thermally most stable gels are obtained with 1-propanol as the solvent.

For both polymer gels[13] and organogels,[14,15][15] the concentration dependence of the gel−sol phase transition temperature has often been analyzed by means of the van't Hoff relationship.[16,17] If it is assumed that the gel−sol transition is a reversible process and that the equilibrium constant of this process is linearly proportional to the critical gelation concentration, the van't Hoff relationship yields the enthalpy of the gel−sol phase transition according to eq 1.

$$\frac{\mathrm{d}\ln(C_g)}{\mathrm{d}(1/T_g)} = -\frac{\Delta H_g}{R} \qquad (1)$$

Although previously no satisfying correlation was obtained for gels of **1** with, for instance, aromatic solvents,[8c] the concentration dependence of the gel−sol phase-

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Table 1. Summary of Thermotropic Properties of Gels of 1 with Primary Alcohols[a]

solvent	T_g[b]	$C_g(20)$[c]	ΔH_g	T_{on}[d]	T_{max}[d]	T_{end}[d]	ΔH_m[d]
propanol	39	2.8 ± 0.5	78 ± 2	20	39	50	56 ± 2
butanol	34	4.5 ± 0.5	72 ± 2	15	37	43	50 ± 2
hexanol	32	5.7 ± 0.5	70 ± 4	11	33	39	49 ± 2
octanol	34	4.3 ± 0.5	73 ± 2	11	31	37	42 ± 2

[a] All temperatures and enthalpies are given in °C and kJ/mol, respectively. [b] T_g at a concentration of 19 mM. [c] $C_g(20)$ is the critical gelation concentration (in mM) at 20 °C, calculated by using eq 1. [d] At an average concentration of 25 mM (for exact concentrations, see Figure 3). T_{on}, T_{max}, and T_{end} are the temperatures of the onset, maximum, and end, respectively, of the endothermic transition measured by DSC.

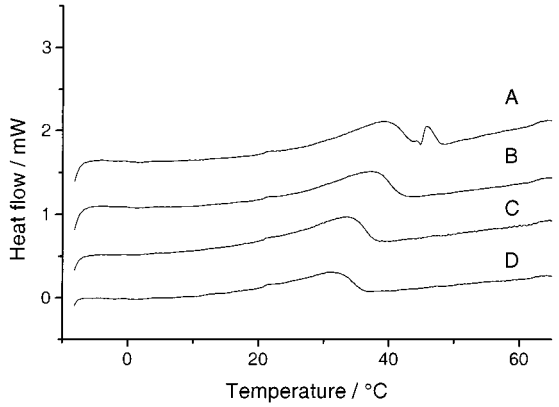

Figure 3. Differential scanning calorimetry (heating scans) of gels of **1** with 1-propanol (A, [**1**] = 22.8 mM), 1-butanol (B, [**1**] = 24.5 mM), 1-hexanol (C, [**1**] = 25.4 mM), and 1-octanol (D, [**1**] = 25.6 mM). Heating rate was 5 °C/min.

transition temperatures of gels of **1** with the primary alcohols studied here could very well be described by the van't Hoff relationship (Figure 2b). The resulting enthalpies are summarized in Table 1, together with the critical gelation concentrations at room temperature. The values of ΔH_g and T_g in Table 1 reveal that gels of **1** in octanol, hexanol, and butanol are equally stable. However, the thermal stability of propanol gels is significantly better, which is reflected in both a higher ΔH_g and a higher T_g. The differences in the critical gelation concentrations, C_g, at room temperature are more pronounced, and follow the trend hexanol > octanol ∼ butanol > propanol.

Figure 3 shows the heating scans for gels of **1** with the various alcohols as measured by DSC. For octanol, hexanol, and butanol gels, a single but very broad endothermic transition was observed during heating, indicating that this is a less cooperative transition. Also, for propanol gels, a broad endothermic transition was obtained, but for this solvent an additional small endothermic transition at 45 °C was observed. The origin of this latter transition is not clear.[18]

It is important to note that the gel−sol phase-transition temperature, T_g, as obtained by the dropping-ball method does not correlate to either the onset, maximum, or end of the transition as observed by DSC. The main transition starts well below the gel−sol transition temperature, T_g, but also continues to temperatures higher than T_g (Table 1). Most likely by means of DSC, the complete transition from a heterogeneous gel state to a homogeneous solution is observed, in analogy to the melting transition of molecular crystals in equilibrium with a saturated solution.[16] The gel−sol phase transition temperature, T_g, on the other hand, is most likely the temperature at which the number density of fibers drops below the critical density for network formation.[13,19] For this same reason it also is not possible to directly compare ΔH_g and ΔH_m, obtained from the dropping-ball and DSC experiments, respectively.

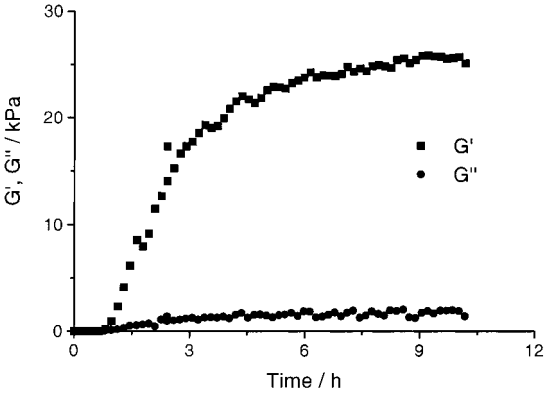

Figure 4. Variation of G' (■) and G'' (●) with gelation time for a 19 mM bis-urea solution in 1-hexanol. Stress amplitude $\sigma_0 = 50$ Pa.

Whereas T_g clearly depends on the aging time, it was observed that the shape of the DSC melting transition is not significantly influenced by aging, and that the enthalpy of the transition does not increase by more than 10% after aging for 15 h at −10 °C. Apparently, aging has a less pronounced effect on the melting transition than on the gel−sol transition temperatures, T_g. On the other hand, the differences between gels of **1** in the different solvents are much more evident, and most markedly, both the maximum temperature of the transition (T_m) and the enthalpy, ΔH_m, consistently increase with increasing polarity of the solvent.

Rheological Properties of the Gels. The gelation of alcohols by **1** is caused by the self-assembly of **1** into an entangled network structure. Because the dynamics and strength of the network structure determine the viscoelastic properties, the alcohol gels of **1** that were the subject of this study were further characterized by rheology.

In a first series of experiments, gel formation was followed by measuring the dynamic moduli (G' and G'') as a function of time. As an example, Figure 4 shows results obtained for a 19 mM solution of **1** in 1-hexanol. Initially, G' and G'' are very small quantities ($\ll 1$ Pa), indicating that the system behaves as a viscous liquid. After a lag time (ca. 1 h), G' starts to increase rapidly with time and becomes much larger than G'', indicating the formation of a network structure. After several hours a plateau region develops, where both components of the modulus become constant or increase very slowly with time.

Figure 5 shows the variation of the plateau value G^∞ with gelator concentration c for various primary alcohols. As expected, G^∞ increases with increasing gelator concentration. The plateau value G^∞ also depends on the type of alcohol used, and at a fixed gelator concentration, G^∞

(17) A rigorous application of the van't Hoff law would involve the use of activity coefficients to describe nonideal behavior of the solvent. This requires, however, the melting temperature and enthalpy of the pure substance, which could not be obtained because of thermal decomposition of **1** upon melting. See also, for instance, Williams-Seton, L.; Davey, R. J.; Lieberman, H. F. *J. Am. Chem. Soc.* **1999**, *121*, 4563−4567.

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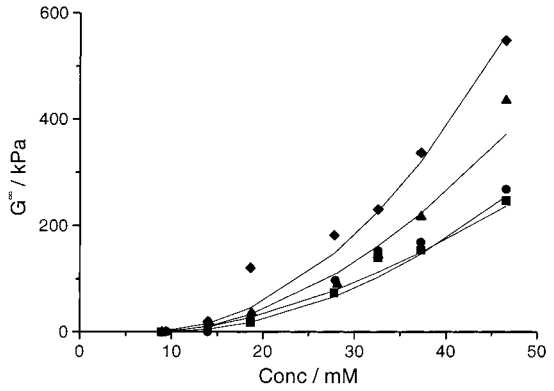

Figure 5. Variation of G^∞ with bis-urea concentration in 1-octanol (■), 1-hexanol (●), 1-butanol (▲) and 1-propanol (◆). Drawn lines are best fits to $G^\infty \sim (c-c_0)^p$.

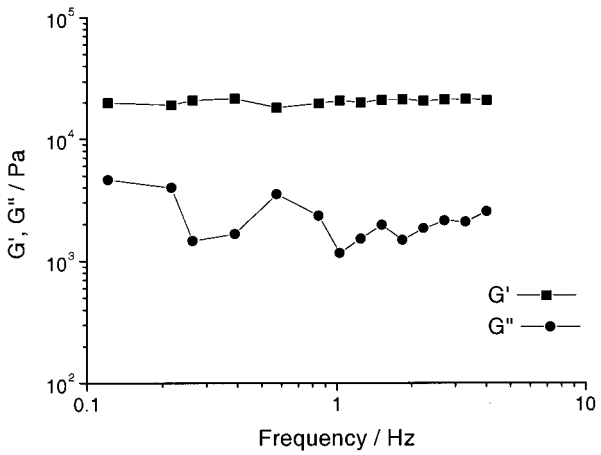

Figure 6. Variation of G' (■) and G'' (●) with oscillation frequency for a 19 mM bis-urea gel in 1-hexanol. Stress amplitude $\sigma_0 = 50$ Pa.

increases in the order 1-octanol < 1-hexanol < 1-butanol < 1-propanol. Apparently, the solvent dependency of the elastic modulus follows the same order as the thermal stability. The variation of G^∞ with gelator concentration could be described by a power-law expression of the form $G^\infty \sim (c - c_0)^p$. The minimum gelator concentration, c_0, at which gelation is observed is 6.5−8.5 mM, depending on the type of alcohol used. Figure 5 shows best fits of this expression to the experimental data, with $c_0 = 8.5$ mM and $p = 1.6$ (1-octanol), $c_0 = 8.5$ mM and $p = 2.0$ (1-hexanol), $c_0 = 8.5$ mM and $p = 1.8$ (1-butanol), and $c_0 = 6.5$ mM and $p = 2.1$ (1-propanol). The minimum gelation concentrations thus determined are in good agreement with the values obtained from the dropping-ball experiments.

In general, dynamic moduli depend on the frequency (time scale) of the measurement. The observed frequency dependence may give insight into the relaxation and lifetime of the bonds between the particles forming a network. If the bonds have a permanent character, only a small frequency dependence is expected and $G' > G''$ at all frequencies. On the other hand, if the bonds have a temporary character, a significant frequency dependence can be observed, with $G' < G''$ at low frequencies and $G' > G''$ at high frequencies.[9,20] Figure 6 shows the frequency response of a bis-urea gel in 1-hexanol (10 h after preparation). As is seen from the figure, the moduli do not depend strongly on oscillation frequency in the frequency range tested (0.1−4 Hz), and $G' \gg G''$ at all frequencies. The frequency response is typical for gels with permanent bonds, and has been observed for, e.g., organogels of a benzhydroxamic acid derivative[21] and cyclohexanol derivatives.[15] Similar results were obtained for gels of **1** with the other primary alcohols studied in this paper.

Dynamic moduli were measured as a function of stress amplitude to determine the linear regime of a 19 mM bis-urea gel in 1-hexanol (i.e., the regime where G' and G'' are independent of the stress amplitude and reflect the properties of the unperturbed network). It was observed that the modulus of the gel is almost independent of the applied stress up to ca. 100 Pa (corresponding to a deformation $\gamma \cong 0.004$). At higher stresses a sharp decrease of G' is observed, which is attributed to (partial) breakup of the gel network structure. Unfortunately, the occurrence of slip between the sample surface and the wall of the measurement cell could not be excluded at these higher stresses. It is not possible, therefore, to determine the fracture stress of the gel (i.e., the stress at which $G' = G''$) in a reliable way.

Outside the linear regime, mechanical stresses cause damage to the gel network structure. Some recovery of gel structure may take place after the shear stress is removed. To determine the extent and rate of the recovery process, we performed the following experiment. Bis-urea gels were grown in a beaker (50 mL) and aged for ca. 24 h. The gel structure was then disrupted by stirring with a spatula. Stirring continued until a liquid (pourable) dispersion of submillimeter particles was obtained. The dispersion was poured into the measuring cell of the rheometer, and G' was measured as a function of time. Even for a gel of **1** in 1-hexanol at a concentration as low as 19 mM, a fast initial increase of G' was observed, and an equilibrium value was reached after approximately 1 h. The equilibrium value of G' ($\approx$ 40 kPa) is approximately equal to the plateau value of the undisturbed bis-urea gel in 1-hexanol at the same gelator concentration (see Figure 5). Apparently, the loss of gel structure is highly reversible. This reversibility is an important property when bis-urea compounds are used as gelling agents in industrial applications.

It is interesting to note that in all cases, the gelation of alcohols by **1** is characterized by an induction time, t_0. With the dynamic modulus experiments the temperature equilibration is, however, too slow to allow a reliable measurement of the induction times from the data shown in Figure 4. In an alternative experiment, the gelling times, t_{gel}, were determined, i.e., the time at which solution no longer flowed after being cooled to room temperature. These gelling times can easily be determined by visual inspection of gelling solutions. Figure 7 shows the variation of the gelling time, t_{gel}, with the inverse gelator concentration for various primary alcohols. A linear relationship is seen to exist between $1/t_{gel}$ and the concentration. From the results shown in Figure 7, it is clear that the gelling time is dependent on the type of alcohol used. At fixed gelator concentration, gelling times decrease in the order 1-octanol > 1-hexanol > 1-butanol > 1-propanol.

Another problem associated with studying the early stages of gel formation by rheology (dynamic modulus measurements) is that directly after preparation of a bis-urea solution, G' and G'' are very small quantities ($\ll$1 Pa) and cannot be measured reliably with the equipment used. To characterize the rheological properties of the system before gelation (i.e., at $t < t_{gel}$), steady-shear viscosity measurements are performed. Figure 8 shows

(20) Ross-Murphy, S. B. *Food Hydrocolloids* **1987**, *1*, 485−495.

(21) Terech, P.; Coutin, A.; Giroud-Godquin, A. M. *J. Phys. Chem. B* **1997**, *101*, 6810−6818.

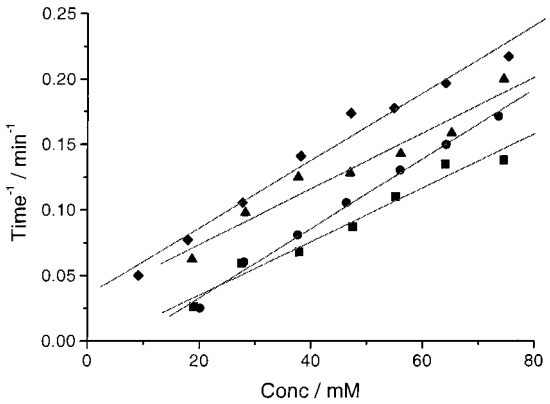

Figure 7. Variation of gelling time, t_{gel}, with bis-urea concentration in 1-octanol (■), 1-hexanol (●), 1-butanol (▲) and 1-propanol (◆). Gelling times were determined by visual inspection of gelling solutions.

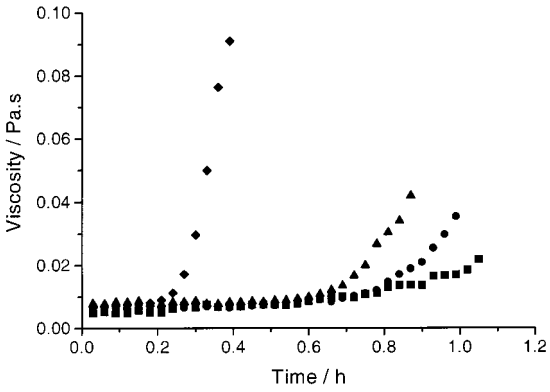

Figure 8. Viscosity of a 9 mM bis-urea solution in 1-hexanol as a function of time. Shear rate: 5 s^{-1} (■), 15 s^{-1} (●), 25 s^{-1} (▲) and 100 s^{-1} (◆).

the viscosity as a function of time for a 9 mM bis-urea solution in 1-hexanol at various (constant) shear rates. Immediately after the solution is prepared, viscosity is equal to that of the pure alcohol ($\eta \approx 5$ mPa.s). The viscosity increases with time as a result of aggregation of bis-urea molecules into fiberlike structures during the first stage of the gelation process. Interestingly, the viscosity increase is faster at higher shear rates. The shear rates applied in the measurement are too low to affect the aggregation behavior of the individual bis-urea molecules (i.e., Peclet numbers are less than unity).[22] To explain the effect on viscosity, we assume that shear promotes the aggregation of bis-urea fibers into larger structures. It is expected that the aggregation of fibers is promoted only in the initial stage of the process. When the aggregates become too large, shear forces will prevent further growth and inhibit the formation of a gel.

Conclusions

The bis-urea gelling agent **1** forms thermoreversible gels with various primary alcohols.[7a,8c] Electron microscopy studies have shown that gel formation is due to aggregation of **1** into long fibers, which in turn associate to form an entangled network structure. The gel properties were further investigated by rheology measurements. The experiments show that with these alcohols, bis-urea compound **1** forms fairly rigid gels up to concentrations of at least 50 mM. The rheology experiments further reveal that for all solvents investigated, the gels behave as viscoelastic solids, which is due to the static nature of the network structure on the time scale of these experiments, i.e., less than 100 s. In this regard it is remarkable that the gel state is spontaneously restored after being disrupted to a viscous fluid by mechanical agitation. The thixotropic behavior can most likely be attributed to a much more dynamic character of the gel network on the significantly larger time scale of these particular experiments, i.e., ranging from minutes to hours.

Interesting observations were made with regard to the solvent dependency of both the thermotropic and the rheological properties of gels of **1**. From the phase diagrams of the gel systems and the DSC experiments, it is clear that the thermal stability of gels of **1** increases in the order 1-octanol < 1-hexanol < 1 butanol < 1-propanol, nicely corresponding to increasing polarity of the solvent. This result is counterintuitive because we expected hydrogen-bond formation between urea groups to be the primary driving force for aggregation, and hence a decrease in the thermal stability of gels of **1** with increasing solvent polarity. This was indeed the case when we compared the thermal stability in DMSO and *p*-xylene, and moreover, we also observed that cyclohexyl-based bis-ureas in which the linear dodecyl chain is replaced by a branched alkyl chain did not gelate ethanol or even 2-propanol.[8c] Apparently, for aggregation of **1** in more polar solvents, solvophobic interactions become dominant over hydrogen-bonding interactions, which can be attributed to the presence of the two dodecyl chains in **1**.

The solvent dependence of the rheological properties follows the same trend, i.e., the stability and strengths of the gels increase with the solvent polarity. These different rheological properties of the gels could originate from different network morphologies or from different strengths of intermolecular interactions at the junction zones, or from a combination of both. Although it was shown previously that the solvent can have a pronounced influence on the morphology,[8] the electron micrographs did not show significant differences in the morphology of gels of **1** with the primary alcohols studied here. It is therefore tempting to assume that the increased network stability and strength in more polar solvents is due at least partly to increased strength of the junction zones in more polar solvents, and hence, that these junction zones are most likely stabilized by solvophobic forces. This conclusion is consistent with the model for the molecular arrangement of **1** previously proposed.[8c] In this model, the urea moieties form a hydrogen-bonded network parallel to the long fiber axis, and the cyclohexyl groups and aliphatic chains are exposed at the fiber−solvent interface. In this model, two or more fibers can join to form a junction zone which then is not only stabilized by van der Waals interactions between the hydrophobic fiber surfaces, but is also partly driven by liberation of polar solvent molecules from these surfaces.

Although the kinetics of the gelation process was not studied in detail, some preliminary conclusions can already been drawn from these first results. The dropping-ball experiments, the gelation times, and the rheology experiments all clearly showed that the gelation of the primary alcohols by **1** is rather slow process which can take more than hours, and which furthermore is characterized by an induction time. Gelation by **1** is probably a multistep process. A tentative mechanism would be that in a first step the urea molecules aggregate into small, thin fibers, causing an initial increase in the viscosity. In the second step, the small fibrous aggregates combine to form a network structure in the solvent, thereby causing gelation

(22) For example: van de Ven, T. G. M. *Colloidal Hydrodynamics*; Academic Press: London, 1989.

of the liquid. Again, the rate of gelation shows the same dependence on the polarity of the solvent as was found for the thermal and mechanical stability of the gels, i.e., it increases with increasing solvent polarity. This dependence can be explained by assuming that the primary aggregation process has much in common with the crystallization of solids from solution, which involves nucleation as the rate-limiting step. In the systems studied here, the solubility of **1** decreases with increasing solvent polarity. Hence, the supersaturation will increase and therefore, so will the rate of nucleation.

In conclusion, by combining thermotropic and rheological studies on organogels of bis-urea compound **1**, we have obtained new insights into the relationship between the thermotropic and viscoelastic properties of the gel and the properties of the solvent. Comparison of the gel properties in closely related solvents such as the alcohols studied here has made it clear that even with strongly hydrogen-bonding gelling agents, such as the bis-urea compound studied here, solvophobic interactions can be dominant in more polar solvents. Solvophobic effects are also known to play a role in very apolar solvents, i.e., hydrocarbons gelated by perfluorocarbon−hydrocarbon block compounds,[23] and are probably of primary importance in many other gel systems as well.

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